

Environmental Technology Verification Program

Advanced Monitoring Systems Center

Generic Verification Protocol
for Portable Water Analyzers
for Metals and Other
Inorganics

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GENERIC VERIFICATION PROTOCOL

FOR

**PORTABLE WATER ANALYZERS FOR
METALS AND OTHER INORGANICS**

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ACRONYMS

AMS	Advanced Monitoring Systems
ASTM	American Society for Testing and Materials
EPA	Environmental Protection Agency
ETV	Environmental Technology Verification
HDPE	high-density polyethylene
ICP-MS	inductively coupled plasma mass spectrometry
ID	inside diameter
l	liter
LFM	laboratory-fortified matrix
MCL	maximum contaminant level
MDL	method detection limit
NIST	National Institute of Standards and Technology
PE	performance evaluation
ppb	parts per billion
PT	performance test
QA	quality assurance
QC	quality control
QCS	quality control standard
QMP	quality management plan
RB	reagent blank

1 INTRODUCTION

1.1 Test Description

This protocol provides generic procedures for implementing a verification test of portable analysis technologies that determine various contaminants in water. The verification test is conducted under the auspices of the U.S. Environmental Protection Agency (EPA) through the Environmental Technology Verification (ETV) program. The purpose of the ETV program is to provide objective and quality-assured performance data on environmental technologies, so that users, developers, regulators, and consultants can make informed decisions about these technologies.

The verification tests are coordinated by Battelle, of Columbus, Ohio, which is EPA's partner in the ETV Advanced Monitoring Systems (AMS) Center. The scope of the AMS Center covers verification of monitoring technologies for contaminants and natural species in air, water, and soil. In performing verification tests, Battelle follows the procedures specified in this protocol and complies with the data quality requirements in the "Quality Management Plan for the ETV Advanced Monitoring Systems Center" (QMP).⁽¹⁾

1.2 Test Objective

The purpose of verification tests of portable water analyzers is to quantify the analytical and operational performance characteristics of these technologies. A variety of quality control, performance evaluation, and environmental water samples is analyzed to assess the capabilities of the analyzers relative to accepted reference methods.

1.3 Roles and Responsibilities

The verification test is performed by Battelle with the participation of the vendors whose analyzers are being verified. The chart in Figure 1 shows the organization of responsibilities for Battelle, the vendor companies, and the EPA. Specific responsibilities are detailed below.

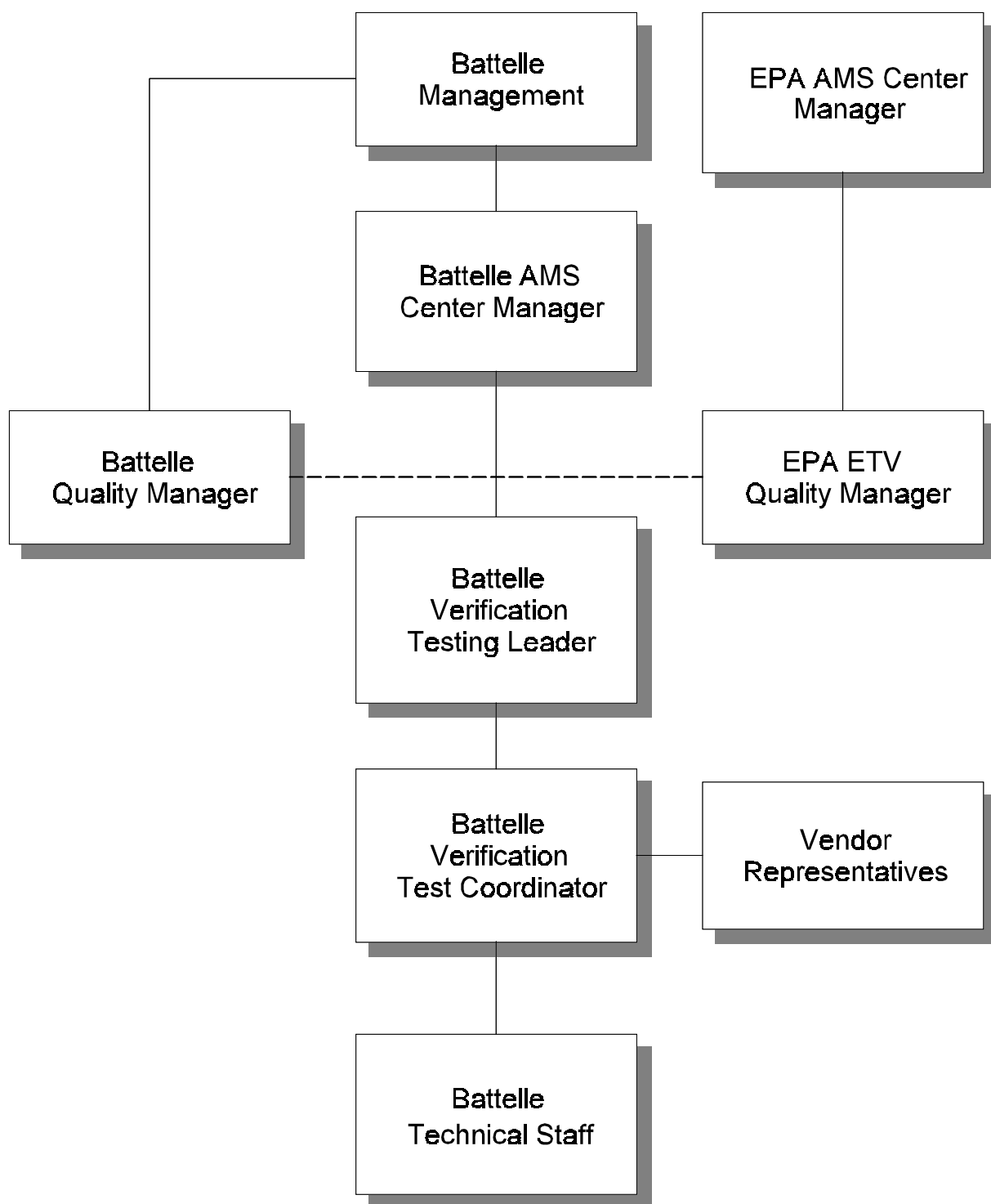


Figure 1. Organization Chart for Portable Water Analyzer Verification Test

1.3.1 Battelle

The Verification Test Coordinator has the overall responsibility for ensuring that the technical, schedule, and cost goals established for the verification test are met. The Verification Test Coordinator shall

- Assemble a team of qualified technical staff to conduct the verification test
- Direct the team in performing the verification test in accordance with the test/quality assurance (QA) plan developed from this protocol
- Ensure that all quality procedures specified in the test/QA plan and in the QMP are followed
- Prepare a draft test/QA plan, verification reports, and verification statements
- Revise the draft test/QA plan, verification reports, and verification statements in response to reviewers' comments
- Coordinate distribution of the final test/QA plan, verification reports, and verification statements
- Respond to any issues raised in assessment reports and audits, including instituting corrective action as necessary
- Serve as the primary point of contact for vendor representatives
- Establish a budget for the verification test and monitor staff effort to ensure that budget is not exceeded
- Ensure that confidentiality of vendor information is maintained.

The Verification Testing Leader for the AMS Center provides technical guidance and oversees the various stages of verification testing. The Verification Testing Leader shall

- Support the Verification Test Coordinator in preparing the test/QA plan and organizing the testing
- Review the draft test/QA plan
- Review the draft verification reports and statements.

The Battelle AMS Center Manager shall

- Review the draft test/QA plan
- Review the draft verification reports and verification statements
- Ensure that necessary Battelle resources, including staff and facilities, are committed to the verification test
- Ensure that vendor confidentiality is maintained
- Support the Verification Test Coordinator in responding to any issues raised in assessment reports and audits
- Maintain communication with EPA's AMS Center Quality Manager.

Battelle Technical Staff shall test the analyzers during the verification test and conduct associated experimental activities. Technical staff shall

- Assist in collecting samples
- Analyze samples for the verification test as described in the test/QA plan.

Battelle's Quality Manager for this verification test shall

- Review the draft test/QA plan
- Conduct a technical systems audit (TSA) once during the verification test
- Audit at least 10% of the verification data
- Prepare and distribute an assessment report for each audit
- Verify implementation of any necessary corrective action
- Issue a stop work order if self-audits indicate that data quality is being compromised; notify Battelle's AMS Center Manager if stop work order is issued
- Provide a summary of the audit activities and results for the verification reports

- Review the draft verification reports and statements
- Have an overall responsibility for ensuring that the test/QA plan is followed.

1.3.2 Vendors

Vendor representatives shall

- Review the draft test/QA plan
- Approve the test/QA plan
- Provide two off-the-shelf models of the analyzers to be verified for the duration of the verification test
- If necessary, instruct Battelle personnel on how to operate and maintain the analyzers prior to testing
- Review their respective draft verification reports and statements.

1.3.3 EPA

EPA's responsibilities in the AMS Center are based on the requirements stated in the "Environmental Technology Verification Program Quality and Management Plan of the Pilot Period (1995-2000)"⁽²⁾ or the most current update of this document. The roles of the specific EPA staff are as follows:

EPA's ETV Quality Manager shall

- Review the draft test/QA plan
- Perform at his/her option one external TSA during the verification test
- Notify the Battelle AMS Center Manager to facilitate a stop work order if an external audit indicates that data quality is being compromised
- Prepare and distribute an assessment report summarizing the results of an external audit
- Review draft verification reports and statements.

The EPA AMS Center Manager shall

- Review the draft test/QA plan
- Approve the final test/QA plan
- Approve the final verification reports
- Review the draft verification statements.

2 VERIFICATION APPROACH

2.1 Scope of Testing

This generic protocol specifically addresses verification testing of (1) portable analyzers that provide quantitative measurements of metals and other inorganic contaminants in water and (2) portable test kits that provide qualitative or semi-quantitative measurements. The quantitative analyzers consist of a portable electronic instrument that often requires a specific reagent solution. Typically the reagent and the water sample are mixed, and the mixture is inserted into the analyzer and probed, either photometrically or electrochemically, to provide a quantitative determination of the target contaminant. Results are reported by a digital display or electronic output signal. Technologies that provide only qualitative results are typically test strips or reagent solutions that, when exposed to the water sample, indicate the presence of the analyte through a visible color change. These approaches are designed primarily to indicate the presence or absence of the target analyte relative to some regulatory or health-based concentration level. Semi-quantitative results can be obtained using these same technologies by comparing the colors to those of standards run with the samples or to a color comparison chart provided by the manufacturer. These comparators typically have discrete color levels that indicate different analyte concentrations, and the results are based on subjective visual comparisons made by the user. In some cases, quantitative results can be obtained by submitting the samples to a laboratory and analyzing them with a colorimeter. Both quantitative and qualitative analyzers are designed to be operated by non-technical users. The analyzers, whether quantitative or qualitative, may detect a variety of aqueous analytes, including dissolved metals and other inorganic cations and anions.

Verifying portable water analyzers involves testing them with known calibration standards and comparing the results with the results of appropriate reference methods. Statistical comparisons of the analytical results from the reference methods and the analyzers being verified provides a basis for quantitative performance evaluations. Each of the analyzers also shall be evaluated in terms of ease of use, cost, and sample throughput.

The quantitative (and semi-quantitative) analyzers measure analyte concentrations and shall be evaluated in terms of

- Accuracy
- Precision
- Linearity
- Method detection limit
- Matrix interference effects
- Operator bias
- Inter-unit reproducibility.

The qualitative analyzers indicate only the presence or absence of a color change associated with a given analyte. The color change can be semi-quantified by comparing it to a color chart. As such, the performance of these analyzers shall be verified in terms of

- Rate of false positives/false negatives
- Lowest calibration concentration producing a positive response
- Highest calibration concentration producing a negative response
- Matrix interference effects
- Operator bias
- Inter-unit reproducibility.

2.2 Experimental Design

The verification test involves challenging the analyzers with a variety of test samples, including a set of fresh water samples and a set of salt water samples representative of those likely to be analyzed using these devices. All samples are analyzed by the analyzers being tested and by an appropriate reference method. The results from the analyzers are compared to those from the reference method to quantitatively assess accuracy, linearity, and detection limit. Multiple aliquots of each test sample are analyzed separately to assess precision. For each analyzer, identical sets of samples are analyzed independently by two separate operators (a technical and a non-technical staff member) to test for operator bias. The analyzers are designed for non-technical operators, and the non-technical staff member shall have little prior knowledge of the analyzer being verified. A vendor representative can serve as the technical operator if desired. Interference and matrix effects are assessed by separately evaluating accuracy, precision, and linearity on distinctly different sample matrices (i.e., prepared, drinking water, fresh water, and salt water samples). Sample throughput is estimated based on the time required to analyze a sample set. Performance parameters, such as ease of use and reliability, are based on documented observations of the operators. Each analyzer shall be used in a field environment, as well as in a laboratory setting, to assess the impact of field conditions on performance. Inter-unit reproducibility is evaluated by comparing results from two units of each analyzer tested.

2.3 Test Samples

Test samples to be used in the verification test include quality control (QC) samples, performance test (PT) samples, and environmental water samples. Tables giving examples of the number and type of samples to be analyzed for selected analytes are provided in Appendix A. The QC and PT samples shall be prepared from purchased standards. The QC sample concentrations for most analytes are targeted to the EPA maximum contaminant level (MCL) for drinking water or other applicable regulatory guidelines. The PT samples range from 10% to 1,000% of that guideline level. Environmental water samples similar to those indicated in Appendix A shall be collected from various drinking water and surface water sources. All samples are analyzed by the

two units of each analyzer undergoing verification and by a laboratory reference method. Every tenth sample is analyzed twice by the reference method to document the reference method's precision.

2.3.1 QC Samples

Prepared QC samples include both laboratory reagent blanks (RB) and laboratory-fortified matrix (LFM) samples. The RB samples are prepared from American Society for Testing and Materials (ASTM) Type II deionized water and exposed to identical handling and analysis procedures as other prepared samples, including the addition of all reagents. These samples are used to help ensure that no sources of contamination are introduced in the sample handling and analysis procedures. The LFM samples are prepared as aliquots of environmental samples and spiked in the field to increase the analyte concentration by the amount shown in the tables in Appendix A. The spike solution used to prepare the LFM is prepared in the laboratory and brought to the field site. These samples are used to help identify whether matrix effects have an influence on the analytical results. At least 10% of all the prepared samples to be analyzed will be RBs, and at least one sample taken from each sampling site will be an LFM.

Quality control standards (QCS) are used as a calibration check to verify that the analyzers being verified and the reference instruments are properly calibrated and reading within defined control limits. These standards shall be purchased from a commercial supplier and shall be subject only to dilution as appropriate. The calibration of all instruments shall be verified using a QCS before and after each testing day, as well as after every tenth sample. Additional standards shall also be purchased from an independent supplier for use in a performance evaluation audit, as described in Section 6.2.1.

2.3.2 PT Samples

In general, two types of PT samples are used in the verification test. All PT samples are prepared in the laboratory using ASTM Type II water as the water source.

One type of PT solution includes only the single analyte at various concentrations and is prepared specifically to help determine the analyzer accuracy, linearity, and detection limit. To

determine the detection limit of the analyzers, a solution with a concentration five times the vendor's reported detection limit is used. Seven non-consecutive replicate analyses of this solution are made to obtain precision data with which to determine the method detection limit (Appendix A). Additionally, solutions are prepared to assess the linearity over a broad concentration range. Four aliquots of each of these solutions are prepared and analyzed separately to assess the precision of the analyzers (Appendix A).

The second type of PT sample to be used in the test helps establish the effects of potential matrix interferences on the performance of the analyzers. These samples are prepared from solutions with known concentrations of the analytes (see Appendix A) and are spiked with potentially interfering species likely to be found in typical water samples. The first sample contains low levels of interferences, which will consist of 1 mg iron, 3 mg sodium chloride, and 0.1 mg of sulfate per liter at a pH of 6. The second sample contains high levels of interferences, which will consist of 10 mg iron, 30 mg sodium chloride, and 1.0 mg of sulfate per liter at a pH of 3. Eight replicate samples of each of these solutions are analyzed.

2.3.3 Environmental Samples

Environmental samples, including tap water (well and community sources), fresh surface water, and salt water shall be collected from a variety of sources and used to evaluate technology performance. A representative sample of water sources includes

- Drinking water (e.g., drinking fountain, community water, well water)
- Fresh water (e.g., rivers, reservoirs)
- Salt water (e.g., estuaries, coast lines).

In all cases, the analyzers being verified are used to analyze the water samples as soon as possible after collection. The results of those analyses are compared to subsequent reference method analyses of the same samples in the laboratory.

Drinking water samples are collected directly from the tap into 2-liter (l) high-density polyethylene (HDPE) containers. The samples will be split into 100-ml aliquots. Four aliquots

of each sample are analyzed at the time of collection by each of the analyzers being verified. Four aliquots of each sample are returned to the laboratory for reference analysis. These aliquots are preserved and stored as appropriate for the target analyte and analyzed within appropriate holding times. If possible, at least one fresh water source should have concentrations of target analyte in the mid range of quantitative analyzers being verified or at least 10 times the vendor-estimated detection limit for qualitative analyzers.

Fresh water samples are collected in 500-ml HDPE containers. The samples are collected at the surface of the water near the shoreline by submerging the containers no more than one inch below the surface of the water. The samples are split into four 100-ml aliquots. Each body of water is sampled at four distinct locations. Two aliquots of each sample are analyzed in the field at the time of collection by the analyzers being verified. One aliquot of each sample is returned to the laboratory for reference analysis for each target analyte. This aliquot will be preserved and stored as necessary for the target analyte and analyzed within appropriate holding times.

Salt water samples are collected using a Rosette system as described, for example, in Battelle Duxbury Operations Standard Operating Procedure No. 5-275.⁽³⁾ Five 100-ml aliquots of each sample are obtained for each analyzer undergoing testing. Samples are collected from the surface of the salt water body and from the sediment/water column interface at four distinct locations. One aliquot of each sample is analyzed at the time of collection by each unit of the analyzer being verified and by each operator. One aliquot of each sample is returned to the laboratory for analysis by the reference method.

Field testing occurs on three separate days. These days do not need to be consecutive. One day is used to collect and test drinking water samples. A second is spent collecting and testing fresh water samples from rivers and reservoirs. A third day is spent collecting salt water samples. In these field testing efforts, the analyzers being verified are transported, handled, and used under normal field conditions as a test of real-world reliability and performance. Field conditions (temperature, humidity, weather conditions) are noted at least twice on each day of field testing.

2.4 Reference Method

Technology verification involves, in part, comparing the results from each analyzer being tested with the results obtained from an appropriate reference method. The reference method chosen for the verification test shall be an EPA standard method for the analysis of water. Samples containing metal ions are analyzed using inductively coupled plasma mass spectrometry (ICP-MS) according to modified EPA Method 200.8.⁽⁴⁾ Samples containing anions are analyzed using ion chromatography (IC) according to modified EPA Method 300.1.⁽⁵⁾ The most recent version of these EPA standard methods should be used. Reference methods promulgated and validated by other recognized standard-setting or regulator organization also may be used.

3 MATERIALS AND EQUIPMENT

In general, the verification test relies on the materials and equipment provided by the vendors. Laboratory and field supplies are described below.

3.1 Laboratory Supplies

The following laboratory supplies are needed for preparing the PT and QC samples:

- ASTM Type II water
- Trace metal grade nitric acid
- 1-L, 250-ml, and 100-ml Class A volumetric flasks
- 10-ml Class A volumetric pipets
- 0.5-ml and 1.0-ml micropipets
- Micropipet tips
- National Institute of Standards and Technology-(NIST-) traceable reference standard for target analyte
- 100-ppm iron standard

- Sodium chloride
- Sodium sulfate
- HDPE containers
- pH meter or strips capable of reading pH levels of 6 and 3.

3.2 Field Supplies

The following supplies are needed for collecting field samples:

- ASTM Type II water
- 125-ml, 500-ml, and 1000-ml HDPE containers
- 1-ml micropipet
- 1-ml micropipet tips
- 100-ml HDPE volumetric flasks
- Coolers and blue ice packs for sample storage
- Thermometer (to determine air and water temperature).

3.3 Reference Instrument

The reference method for analysis of metals is performed on a Perkin Elmer Sciex 6000 ICP-MS or equivalent. The reference method for anions is performed on a Dionex 600 Ion Chromatograph or equivalent.

4 PROCEDURES

4.1 Test Sample Preparation and Storage

QC and PT samples are prepared from commercially available NIST-traceable standard solutions. Purchased solutions are diluted to appropriate concentrations using ASTM Type II water in Class A volumetric glassware. In some cases, additional species are added to the solutions to assess the effect of interferences on the performance of the analyzers. These interferences are added to simulate levels of contaminants that may be found in typical water sources. The QC and PT samples shall be prepared within two days of analysis and stored at approximately 4°C until use.

Environmental water samples are collected from the sources indicated in Section 2.3.3 and stored in HDPE containers. Samples are analyzed at the time of collection by the analyzers being verified. The samples to be analyzed by the reference methods are stored at 4°C until analysis and preserved with nitric acid at a pH of less than 2 for metal analytes. The reference analyses shall be performed within the holding times specified in the reference methods, or the field sampling will be repeated.

4.2 Sample Identification

Aliquots to be analyzed are drawn from the prepared standard solutions or from environmental samples and placed in uniquely identified sample containers for subsequent analysis. The sample containers are identified by a unique identification (ID) number. A master log of the samples and sample ID numbers for each analyzer shall be kept. The ID number, date, person collecting, sample location, and time of collection is recorded on a chain-of-custody form for all field samples.

4.3 Sample Analysis

4.3.1 Reference Method

The reference instrument is operated according to the recommended procedures in the instruction manual, and samples are analyzed according to an appropriate reference method. Analysis for metals is conducted according to EPA Method 200.8, “Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma—Mass Spectrometry.”⁽⁴⁾ Analysis for anions is performed using EPA Method 300.1, “Determination of Inorganic Anions by Ion Chromatography.”⁽⁵⁾

Results from the reference analyses shall be recorded electronically and compiled by the laboratory performing the analyses into a report format, including the sample ID and the analyte concentration for each sample.

4.3.2 Analyzers Undergoing Verification

Vendors are required to provide two units of their portable water analyzers. Each unit shall be subjected to the test procedure independently and separate verification results reported for each unit. Those results are then compared to assess inter-unit reproducibility. Each of the analyzers being verified shall be used to analyze the full set of samples for the target analyte chosen by the vendor. As shown in Appendix A, the sample set includes replicates of each of the PT, QC, and environmental samples. The complete set of samples shall be analyzed twice for each of the analyzers—once by a non-technical Battelle staff member and once by a technical staff member using the same sample aliquot. The analyses are performed according to the manufacturer’s recommended procedures as described in the user’s instructions or manual for the analyzer. Calibration and maintenance of the analyzers shall be performed as specified by the manufacturer.

Results from the analyzer being verified shall be recorded manually by the operator on appropriate data sheets. In addition to the analytical results, the data sheets shall include records of the time required for sample analysis and operator observations concerning the use of the analyzer (e.g., frequency of calibration, ease of use, maintenance).

4.4 Schedule

A typical verification test requires approximately five days. Table 1 gives a sample schedule for the activities to be conducted. The time period for each activity should be considered approximate. Some activities may take longer than one day to complete. The samples referred to in Table 1 are those listed in Appendix A.

All participating analyzers in a single verification test shall undergo testing on the same days. The samples analyzed by the instruments undergoing testing also are analyzed by the reference method. All analyzers being tested for a given analyte are challenged with the same set of samples. Separate aliquots are drawn from a single sample for each type of technology. No direct comparison is made between the results from different analyzers; however, it is to the benefit of potential users of the analyzers that test conditions be as similar as possible.

Table 1. Schedule of Verification Test Days

Test Day	Testing Location	Activity
Day One	Laboratory	Analysis of PT samples and associated QC samples with operator #1.
Day Two	Laboratory	Analysis of PT samples and associated QC samples with operator #2.
Day Three	Field Location	Collection and analysis of environmental samples and LFM samples from three drinking water sources.
Day Four	Field Location	Collection and analysis of environmental samples and LFM samples at four locations within three fresh water sites.
Day Five	Transport	Shipping and handling of analyzers undergoing verification to field test site.
Day Six	Field Location	Collection and analysis of environmental samples and LFM samples at salt water locations; shipping of environmental samples to Columbus for subsequent reference analysis.

Participating vendors shall provide their analyzers to laboratory staff one week before the start of testing, so that the staff may become familiar with the units before testing begins. This period also will be used to resolve any questions about analyzer operation or maintenance. Vendor staff may need to be present for this familiarization stage to provide training in operating

the analyzers. If the vendor is serving as the technical operator, vendor staff should be present throughout the testing period. Vendors are encouraged to observe the tests. Analyzers and associated equipment (if not consumables) shall be returned to the vendors at the completion of testing.

5 DATA HANDLING AND REPORTING

5.1 Data Acquisition and Review

A variety of data are acquired and recorded electronically or manually by laboratory staff during the verification test. Operational information, required maintenance, and results from the verification test, as well as sampling procedures, generally shall be documented on data sheets or in laboratory record books. Results from the reference instruments are compiled in electronic format.

Records received or generated by laboratory staff in the verification test receive a one-over-one review within two weeks after receipt or generation before these records are used to calculate, evaluate, or report verification results. These records may include electronic records, laboratory record books, sampling records from the field test, or equipment calibration records. This review is performed by a technical staff member involved in the verification test, but not the staff member that originally received or generated the record. The review is documented by the person performing the review by adding his/her initials and date to a hard copy of the record being reviewed. This hard copy is then returned to the staff member who received, generated, or will be storing the record.

In addition, data calculations performed by Battelle are spot-checked by technical staff to ensure that calculations are performed correctly. Calculations to be checked include reference analysis results and statistical calculations described in this protocol.

The data obtained from the verification test are compiled and reported independently for each analyzer being verified. The results from one vendor's analyzer are not compared to the results from another vendor's analyzer. However, the results for the duplicate analyzers from each vendor are compared.

5.2 Statistical Calculations

5.2.1 Accuracy

Accuracy of the analyzers being verified shall be assessed relative to the results obtained from the reference analyses. Samples are analyzed by both the reference method and the analyzers being verified. The results for each set of analyses are averaged, and the accuracy is expressed in terms of a relative average bias (B) as calculated from the following equation:

$$B = \frac{\overline{d}}{\overline{C}_R} \times 100 \quad (1)$$

where \overline{d} is the average difference between the readings from the analyzer being verified and those from the reference method, and \overline{C}_R is the average of the reference measurements.

Accuracy is assessed independently for each analyzer to determine inter-unit reproducibility. Additionally, the results are analyzed independently for the readings obtained from the two operators to determine if operator bias exists.

5.2.2 Precision

The standard deviation (S) of the results for the replicate samples shall be calculated and used as a measure of instrumental precision at each concentration.

$$S = \left[\frac{1}{n-1} \sum_{k=1}^n (C_k - \overline{C})^2 \right]^{1/2} \quad (2)$$

where n is the number of replicate samples (see tables in Appendix A), C_k is the concentration measured for the k^{th} sample, and \overline{C} is the average concentration of the replicate samples. The instrumental precision at each concentration is reported in terms of the relative standard deviation (RSD), e.g.,

$$RSD = \left| \frac{S}{\overline{C}} \right| \times 100 \quad (3)$$

5.2.3 Linearity

Linearity shall be assessed by linear regression, with the analyte concentration measured by the reference method as the independent variable and the reading from the analyzer being verified as the dependent variable. Linearity is expressed in terms of the slope, intercept, and the coefficient of determination (r^2).

5.2.4 Method Detection Limit

The method detection limit (MDL)⁽⁶⁾ for each analyzer shall be assessed from the seven replicate analyses of a fortified sample with an analyte concentration of five times the vendor's estimated detection limit. The MDL is calculated from the following equation:

$$MDL = t \times S \quad (4)$$

where t is the Student's value for a 99% confidence level, and S is the standard deviation of the replicate samples. The MDL values for the two units of each analyzer are reported as separate results.

5.2.5 Matrix Interferences

The effect of interfering matrix species on the response of an analyzer to a given analyte shall be calculated as the ratio of the difference in analytical response to the concentration of interfering species. For example, if adding 500 parts per billion (ppb) of an interfering species results in a difference of 10 ppb in the analytical result, the relative sensitivity of the analyzer to that interferent is calculated as $10 \text{ ppb}/500 \text{ ppb} = 2\%$.

5.2.6 Operator Bias

To assess operator bias for each analyzer, the results obtained from each operator shall be compiled independently and subsequently compared. The existence of statistically significant operator bias is assessed through a *t*-test of the data.

5.2.7 Inter-Unit Reproducibility

The results obtained from two identical units of each analyzer shall be compiled independently for each analyzer and for each operator and compared to assess inter-unit reproducibility. The results are interpreted using a *t*-test to assess if significant differences exist between the units tested.

5.2.8 Rates of False Positives/False Negatives

The rates of false positives/false negatives of the qualitative analyzers for each analyte shall be assessed relative to the guidance level. Analytes reported as being above that level by the analyzer being verified, but below that level by the reference method, are considered a false positive. Analytes not reported as being above the guidance level by the analyzer being verified, but reported as above that level by the reference method, are considered a false negative. The rate of false positives/false negatives is expressed as a percentage of total samples analyzed for each matrix.

5.3 Data Review

Records generated in the verification test shall receive a one-over-one review within two weeks after generation, before these records are used to calculate, evaluate, or report verification results. Table 2 summarizes the types of data to be recorded. These records may include laboratory record books or reference method analytical results. This review is performed by a Battelle technical staff member involved in the verification test, but not the staff member that originally generated the record. EPA/contractor and/or vendor staff shall be consulted as needed

to clarify any issues about the data records. The review is documented by the person performing the review by adding his/her initials and date to a hard copy of the record being reviewed. This hard copy is returned to the Battelle staff member who generated or who will be storing the record.

5.4 Reporting

The data obtained in the verification test shall be compiled for each vendor's analyzer, and the statistical evaluations described in Section 5.2 shall be applied to each data set without reference to any other. At no time will data from one vendor's analyzer be compared to another

Table 2. Summary of Data Recording Process for the Verification Test

Data to be Recorded	Responsible Party	Where Recorded	How often Recorded	Disposition of Data^a
Dates, times of test events	Battelle	Laboratory record books	Start/end of test, and at each change of a test parameter.	Used to organize/check test results; manually incorporated in data spreadsheets as necessary.
Test parameters (temperature, analyte/interferant identities and concentrations, gas flows, etc.)	Battelle	Laboratory record books	When set or changed, or as needed to document stability.	Used to organize/check test results, manually incorporated in data spreadsheets as necessary.
Reference method sampling data	Battelle	Laboratory record books	At least at start/end of reference sample, and at each change of a test parameter.	Used to organize/check test results; manually incorporated in data spreadsheets as necessary.
Reference method sample analysis, chain of custody, and results	Battelle	Laboratory record books, data sheets, or data acquisition system, as appropriate	Throughout sample handling and analysis process	Transferred to spreadsheets

^a All activities subsequent to data recording are carried out by Battelle.

vendor's analyzer. Following completion of the statistical evaluations, a draft verification report describing the verification test procedures and documenting the analyzer's performance is prepared for each vendor's analyzer. The draft verification reports are each submitted to the

respective vendors for review and comments. The comments provided by vendors on their draft verification reports are the basis for revising the report. The revised reports are submitted to EPA and assigned AMS Center stakeholders for peer review, revised to address peer review comments, and submitted for final EPA approval.

Verification statements for each analyzer are prepared in parallel with preparation of the verification reports. The verification statement is a two- to three-page summary of the technology, the test procedures, and the test results. Draft verification statements are submitted to vendors for review and follow the same review and revision process as the reports. Upon approval by EPA, each verification statement is signed by a senior manager of Battelle and by an EPA laboratory director. Final verification reports and statements will be posted on the ETV Web site (<http://www.epa.gov/etv/centers/center1.html>), and original signed verification statements are provided to the vendors for use in marketing their products.

6 QUALITY ASSURANCE/QUALITY CONTROL

The QA/QC activities associated with the verification test focus primarily on reference analysis, sample preparation and handling, and data recording and analysis. An independent audit covering each of these areas shall be performed by the Battelle Quality Manager to ensure the quality of the verification test.

6.1 QC of Reference Method

Analysis of QC samples throughout the verification test shall be used to document the performance of the reference methods. RB samples shall be analyzed to ensure that no sources of contamination are present. If the analysis of an RB sample indicates a concentration above the MDL for the reference instrument, contamination will be suspected. Any contamination source(s) shall be corrected, and proper blank readings shall be achieved before proceeding with the verification test.

The accuracy of the reference methods shall be verified before and after each testing day, as well as after every tenth sample. The instruments to be used for reference are calibrated

initially according to the procedures specified in the reference method. The instrument calibration is verified using an appropriate QCS. If the QCS analysis differs by more than $\pm 10\%$ from the true value of the standard, the instrument is recalibrated before continuing the test.

LFM samples are analyzed to determine whether matrix effects influence the results of the reference methods. The percent recovery (R) of the spiked solution is calculated from the following equation:

$$R = \frac{C_s - C}{s} \times 100 \quad (5)$$

where C_s is the analyzed concentration of the spiked sample, C is the analyzed concentration of the unspiked sample, and s is the concentration equivalent of the analyte spike. If the percent recovery of an LRM falls outside the range of 85% to 115%, a matrix effect will be suspected.

6.2 Audits

6.2.1 Performance Evaluation Audits

A performance evaluation (PE) audit will be conducted to assess the quality of the reference measurements made in the verification test. A PE audit involves challenging the instruments used for reference methods with standards that are independent of those used to calibrate the instruments for the test. For the PE audit, an independent standard will be obtained from a vendor other than the one that supplied the QC standards. The QC and PE standards will be compared once during the verification test. Agreement of the standards within 10% is required for the measurements to be considered acceptable. Failure to achieve this agreement will trigger recalibration of the instruments with the original QC standards and a repeat of the PE comparison. Failure in the second comparison requires obtaining another set of standards and repeating the performance audit.

6.2.2 Technical Systems Audits

The Battelle Quality Manager shall perform a TSA at least once during the course of the verification test. The purpose of this audit is to ensure that the verification test is being performed in accordance with this protocol and the AMS Center QMP⁽¹⁾ and that all procedures described in this protocol are being followed. During this audit, the Quality Manager reviews reference standards and methods used, compares actual test procedures to those specified in this protocol, and reviews data acquisition and handling procedures. An independent TSA may also be performed by EPA Quality Management staff at EPA's discretion.

6.2.3 Audits of Data Quality

Battelle's Quality Manager shall audit at least 10% percent of the data acquired during the verification test. The Quality Manager traces the data from the initial acquisition, through reduction and statistical analysis, to final reporting, to ensure the integrity of the reported results. All calculations performed on the data undergoing the audit are checked.

6.3 Reporting

Each audit shall be documented in accordance with the for the AMS Center QMP⁽¹⁾ The results of the TSA and the audit of data quality shall be sent to the EPA. Assessment reports include the following:

- Identification of any adverse findings or potential problems
- Corrective actions that address adverse findings or potential problems
- Confirmation by Battelle's Quality Manager that the corrective actions have been implemented and are effective
- Citation of any noteworthy practices that may be of use to others.

6.4 Corrective Action

The Battelle or EPA ETV Quality Managers, during the course of any audit, shall identify to the technical staff performing experimental activities any immediate corrective action that should be taken. If serious quality problems exist, the Battelle Quality Manager is authorized to stop work. Once the audit report has been prepared, the Verification Test Coordinator ensures that a response is provided for each adverse finding or potential problem and implements any necessary follow-up corrective action. The Battelle Quality Manager shall ensure that follow-up corrective action has been taken.

7 REFERENCES

1. "Quality Management Plan (QMP) for the ETV Advanced Monitoring Systems Center," Version 3.0, U.S. EPA Environmental Technology Verification Program, Battelle, Columbus, Ohio, December 2001.
2. "Environmental Technology Verification Program Quality and Management Plan for the Pilot Period (1995-2000)," U.S. EPA, EPA-600/R-98/064, Cincinnati, Ohio, May 1998.
3. "At Sea Collection of Hydrographic Data Using CTD and Rosette," Battelle Duxbury Operations Standard Operating Procedure No. 5-275, January 31, 2000
4. "U.S. EPA Method 200.8, Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma—Mass Spectrometry," Revision 4.4, April 1991.
5. "U.S. EPA Method 300.1, Determination of Inorganic Ions by Ion Chromatography," Revision 1.0, April 1999, *Methods for the Determination of Organic and Inorganic Compounds in Drinking Water*, Volume 1, EPA815-R-00-014, U.S. Environmental Protection Agency.
6. "Appendix B to Part 136—Definition and Procedure for the Determination of the Method Detection Limit, U.S. Code of Federal Regulations, 40 CFR, Part 136.

APPENDIX A

SUMMARY OF TEST SAMPLES FOR SELECTED ANALYTES

Table A-1. Summary of Test Samples^a for Lead

Type of Sample	Sample Characteristics	Concentration	No. of Samples
Quality Control	RB ^b	~ 0	10% of all
	LFM ^b	30 ppb	1 per site
	QCS ^b	30 ppb	10% of all
Performance Test	For the determination of detection limit	Five times the manufacturer's estimated detection limit	7
	Lead	1.5 ppb	4
	Lead	5 ppb	4
	Lead	15 ppb ^c	4
	Lead	45 ppb	4
	Lead	150 ppb	4
	Analyte spiked with interference	45 ppb with low interference	8
	Analyte spiked with interference	45 ppb with high interference	8
Environmental	Drinking fountain	Unknown	4
	Community water	Unknown	4
	Well water	Unknown	4
	Alum Creek Reservoir	Unknown	4
	Olentangy River	Unknown	4
	Scioto River	Unknown	4
	Massachusetts Bay surface water	Unknown	4
	Massachusetts Bay water at sediment/water column interface	Unknown	4

^a Listing is for clarity; samples will be analyzed in random order for the verification testing.

^b See Section 2.3.1 for descriptions of these samples.

^c MCL for lead.

Table A-2. Summary of Test Samples^a for Nitrate

Type of Sample	Sample Characteristics	Concentration	No. of Samples
Quality Control	RB ^b	~ 0	10% of all
	LFM ^b	2 ppm above native level	1 per site
	QCS ^b	2 ppm	10% of all
Performance Test	For the determination of detection limit for nitrate	Five times the manufacturer's estimated detection limit	7
	Nitrate	0.2 ppm	4
	Nitrate	0.6 ppm	4
	Nitrate	2.0 ppm	4
	Nitrate	6.0 ppm	4
	Nitrate	20 ppm	4
	Analyte spiked with interference	3.0 ppm with low interference	8
	Analyte spiked with interference	3.0 ppm with high interference	8
Environmental	Drinking fountain	Unknown	4
	Community water	Unknown	4
	Well water	Unknown	4
	Alum Creek Reservoir	Unknown	4
	Olentangy River	Unknown	4
	Scioto River	Unknown	4
	Massachusetts Bay surface water	Unknown	4
	Massachusetts Bay water at sediment/water column interface	Unknown	4

^a Listing is for clarity; samples will be analyzed in random order for the verification testing.

^b See Section 2.3.1 for descriptions of these samples.

Table A-3. Summary of Test Samples^a for Arsenic

Type of Sample	Sample Characteristics	Concentration	No. of Samples
Quality Control	RB ^b	~ 0	10% of all
	LFM ^b	10 ppb above native level	1 per site
	QCS ^b	10 ppb	10% of all
Performance Test	For the determination of detection limit	Five times the manufacturer's estimated detection limit	7
	Arsenic	1 ppb	4
	Arsenic	3 ppb	4
	Arsenic	10 ppb ^c	4
	Arsenic	30 ppb	4
	Arsenic	100 ppb	4
	Analyte spiked with interference	10 ppb with low interference	8
	Analyte spiked with interference	10 ppb with high interference	8
Environmental	Drinking fountain	Unknown	4
	Community water	Unknown	4
	Well water	Unknown	4
	Alum Creek Reservoir	Unknown	4
	Olentangy River	Unknown	4
	Scioto River	Unknown	4
	Massachusetts Bay surface water	Unknown	4
	Massachusetts Bay water at sediment/water column interface	Unknown	4

^a Listing is for clarity; samples will be analyzed in random order for the verification testing.

^b See Section 2.3.1 for descriptions of these samples.

^c WHO Provisional Guideline Value for arsenic in drinking water.